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RESEARCH ARTICLE

Enhanced mineralization of sulfamethoxazole by gamma radiation in the presence of Fe_3O_4 as Fenton-like catalyst

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Abstract

Antibiotics are becoming ubiquitous emerging contaminants in the aquatic environments due to their large amount of production and extensive application, which have received increasing public concern. In this paper, the degradation and mineralization of sulfamethoxazole (SMX) by ionizing radiation in the presence of Fe_3O_4 as Fenton-like catalyst were evaluated, the influencing factors, such as the initial SMX concentration, initial pH, water matrix, and radical scavenger, etc. were examined. The results demonstrated that SMX could be efficiently degraded. The addition of Fe_3O_4 could improve the degradation efficiency of SMX and increased the dose constant at various SMX initial concentrations. More than 98% of SMX was degraded in Fe_3O_4/gamma radiation system at a wide range of pH (about 3.0–11.0). The mineralization of SMX in the presence of Fe_3O_4 was increased by 200%. Adding free radical scavenger (tert-butyl alcohol) inhibited the degradation of SMX. The addition of Fe_3O_4 enhanced the dose constant of ·OH, indicating that Fe_3O_4 promoted the formation of hydroxyl radicals (·OH) and then improved SMX degradation and mineralization. The degradation efficiency of SMX in secondary effluent of WWTP decreased from 100 to 84% in secondary effluent compared with that in deionized water. The intermediate products during the degradation of SMX by ionizing radiation were identified by high-performance liquid chromatography, and a possible pathway of SMX degradation in such a system was tentatively proposed.

Keywords Advanced oxidation processes · Radiation · Fenton reaction · Sulfamethoxazole · Antibiotics · Magnetite

Introduction

Antibiotics are emerging contaminants in aquatic environments, which have received increasing attention in recent years. Antibiotics can enter into the environment through different sources, including pharmaceutical industry effluent, hospital wastewater, and some livestock farm wastewater (Wang et al. 2019).

Sulfonamides are used for preventing and curing bacterial infectious diseases. They can be added in fodder to prevent diseases and enhance the animal growth. They are widely used around the world due to their stable chemical properties, broad antibacterial spectrum, convenient use, and low price. Among them, sulfamethoxazole (SMX) is widespread used and detected in aquatic environments (Wang and Wang 2018b), such as city canal (Phan et al. 2011), river (Chen and Zhou 2014), sewage treatment plant secondary effluent (Karthikeyan and Meyer 2006), and activated sludge (Gobel et al. 2005). The traditional wastewater treatment processes are not effective for the removal of antibiotics (Gros et al. 2010; Wang and Wang 2016).

Advanced oxidation processes (AOPs) are powerful for the degradation of toxic organic pollutants in water and wastewater (Wang and Xu 2012), which have been gradually applied to degrade antibiotics, such as ozonation (Chen and Wang 2019; Wang and Bai 2017; Dantas et al. 2008), photocatalytic oxidation (Khan et al. 2019; Sayed et al. 2018, 2019), UV/chlorine (Sichel et al. 2011), persulfate oxidation (Rehman et al. 2018; Shah et al. 2018a, 2019; Wang and Wang 2017,

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2018a, 2019), and Fenton-like oxidation (Liu et al. 2018; Shah et al. 2018b; Tang and Wang 2018a, b, 2019; Wan et al. 2016).

Among the stated advanced oxidation processes, ionizing radiation is a promising technique to decompose organic pollutants (Wang and Chu 2016). Decomposition of organic contaminants in aqueous solutions can be performed through direct action and indirect action. As for direct action, high energy rays can directly decompose the organic pollutants. As for the indirect action, water molecules are excited to generate plenty of reactive radicals, including hydroxyl radicals (·OH), hydrated electrons (e_{aq}^-), hydrogen radical (·H), and H_2O_2. The hydroxyl radicals (·OH) is a strong oxidant. The hydrated electrons (e_{aq}^-) is a powerful reductant with − 2.87 V reduction potential in neutral and alkaline condition. And the hydrogen radical (·H) is a strong reductant (Wardman 1989; Trojanowicz et al. 2019). Therefore, organic pollutants can be degraded by oxidation and reduction ways during ionizing radiation.

Ionizing radiation has been used to degrade antibiotics because of its no selectivity and high reactivity (Shen et al. 2019; Yu et al. 2010a, 2010b; Hu and Wang 2007). Shen et al. (2019) found that the removal efficiency of erythromycin A was 86% by ionizing radiation in antibiotic fermentation residues. Chu et al. (2018) demonstrated that with 2.5 kGy irradiation, 0.27 mmol/L penicillin G was completely removed. Liu and Wang (2013) found that the degradation efficiency of sulfamethazine reached 95% at 1 kGy. Sayed et al. (2016) reported that 4.6 mg/L ciprofloxacin was nearly completely decomposed with 870 Gy irradiation. However, the mineralization of antibiotics is difficult by ionizing radiation. Chu et al. (2018) found that with 10 kGy irradiation, TOC removal rate of penicillin G was only 21.7%. Liu and Wang (2013) also found that TOC removal rate of sulfamethazine was 5% with 5 kGy irradiation. Wang and Wang (2018c) reported the TOC removal rate of sulfamethoxazole was 12.8% with 1 kGy irradiation. The industrial application of radiation technology is promising. We have built a demonstration plant for the advanced treatment of textile wastewater using electron beam technology in China in 2017, with the treatment capacity of 2000 m^3/d. The continuous operational experience of 2 years shows that this technology is effective and stable.

Fenton oxidation is a commonly used method of advanced oxidation processes (AOPs), which utilizes the oxidation of Fe^{2+} by H_2O_2 to generate hydroxyl radicals (·OH) at acidic pH condition. Our previous studies found the addition of Fe^{2+} during ionizing radiation could enhancing the antibiotics degradation (Chu et al. 2018; Liu et al. 2014), which may be due to that Fe^{2+} reacting with H_2O_2 which was generated from ionizing radiation to generate ·OH via Fenton reaction, thus improving antibiotics degradation. However, the traditional Fenton reaction is limited to narrow pH range (Mirzaei et al. 2017). Thus, the heterogeneous Fenton-like reaction is widely explored, aiming to expand the feasible operating pH range. Magnetite (Fe_3O_4) has been applied in environmental remediation (Liu and Wang 2019), such as in heterogeneous Fenton-like process for degrading chlorophenol (Xu and Wang 2011, 2012b), phenol and aniline (Zhang et al. 2009), di-azo-aminobenzene (DAB) (Gao et al. 2007), and bisphenol A (Huang et al. 2014). However, no research has been reported about using Fe_3O_4 as a Fenton-like catalyst during gamma radiation to enhance degradation and mineralization of sulfamethoxazole. It is needed to explore the degradation characteristic as well as the mechanism.

The objectives of this study were to explore the degradation and mineralization of sulfamethoxazole (SMX) using gamma radiation with the addition of Fe_3O_4 particles as a Fenton-like catalyst. The effects of initial SMX concentration and pH value on the SMX removal efficiency were studied. TOC removal efficiency at various initial SMX concentrations was also explored. In addition, the dose constant of hydroxyl radicals (·OH) with and without the addition of Fe_3O_4 were also determined. The intermediate products were identified, and the possible pathway for the degradation of SMX was proposed.

Materials and methods

Chemicals

Sulfamethoxazole (SMX, > 98% purity) was obtained from Aladdin Industrial Corporation (China). Fe_3O_4 particles were prepared as follows: $FeSO_4$ (20 mmol/L, 250 mL), and $Fe_2(SO_4)_3$ (20 mol/L, 250 mL) solutions were mixed in round-bottom flask under the protection of argon gas. Then 25%(v/v) ammonia was added dropwise until pH reached 10–11. After stirring for a while, the resulting precipitate was centrifugated for separation of Fe_3O_4 particles. After washing with water and ethanol for three times, Fe_3O_4 particles were freeze-dried for use.

Irradiation experiment

The SMX solution samples were irradiated using a ^{60}Co radiation source, which is located in Tsinghua University. The radioactivity of ^{60}Co gamma-ray source was about 3.6×10^{14} Bq. All SMX aqueous solution samples were preserved in 10-mL glass tubes and irradiated close to the irradiator at ambient temperature. The desired absorbed doses ranging were achieved according to the irradiation time. Fe_3O_4 (0.1 g/L) was added into SMX solution before irradiation to evaluate the influence of Fenton-like catalysts on SMX radiolytic degradation. Different initial concentration of SMX aqueous solution samples was prepared through diluting 200 mg/L SMX stock solution using deionized water, for investigating the impacts of initial concentration on the degradation of SMX. pH value was adjusted by H_2SO_4 and NaOH.

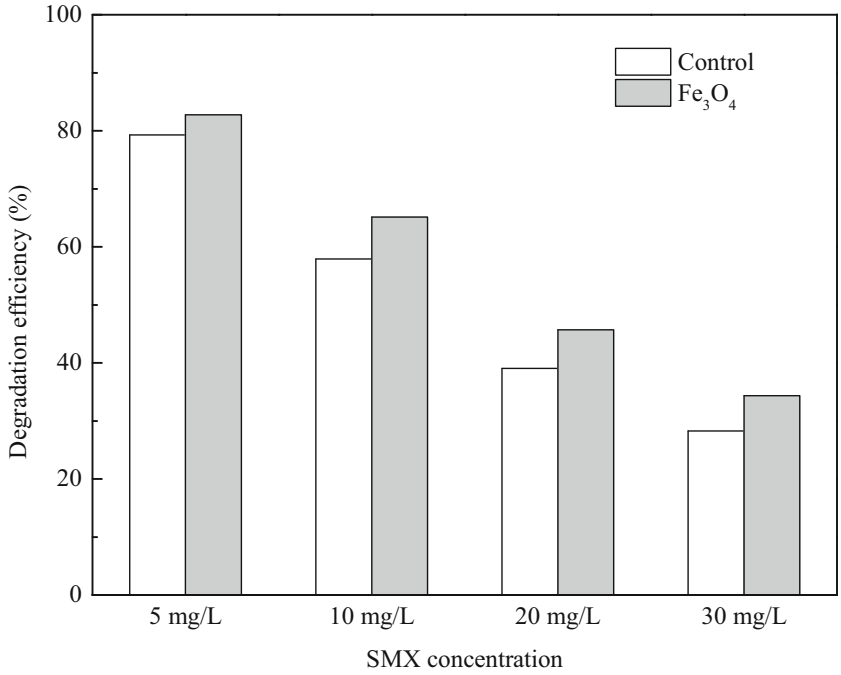


Fig. 1 Degradation efficiency of SMX at different initial concentration with and without the addition of Fe_3O_4. (Dose = 0.2 kGy, $[Fe_3O_4]_{add}$ = 0.1 g/L)

Analytical methods

SMX concentration was determined using high-performance liquid chromatography (1200 Series, Agilent, USA) at the wavelength of 275 ± 10 nm by diode array detector (DAD) (Zhuan and Wang 2019). Total organic carbon (TOC) was determined by a Multi N/C 2100 TOC/TN analyzer (Analytik Jena AG Corporation, Germany). The intermediate products of SMX degradation were determined by LC-MS (Q Exactive, Thermo Scientific).

Results and discussion

Sulfamethoxazole degradation in the presence of Fe_3O_4

Compared with control group which was absence of Fe_3O_4, the addition of Fe_3O_4 could enhance the SMX degradation at various SMX concentration (Fig. 1). During gamma irradiation of SMX aqueous solution, various reactive radical species were formed through water radiolysis, such as ·OH, e_{aq}^- and

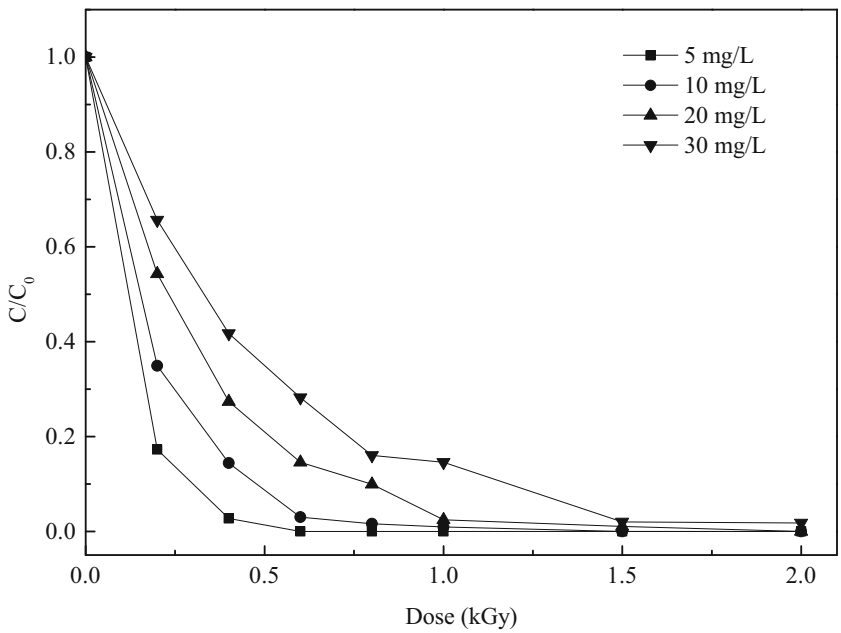


Fig. 2 Degradation of SMX at different initial concentration in the presence of Fe_3O_4. ($[Fe_3O_4]_{add}$ = 0.1 g/L)

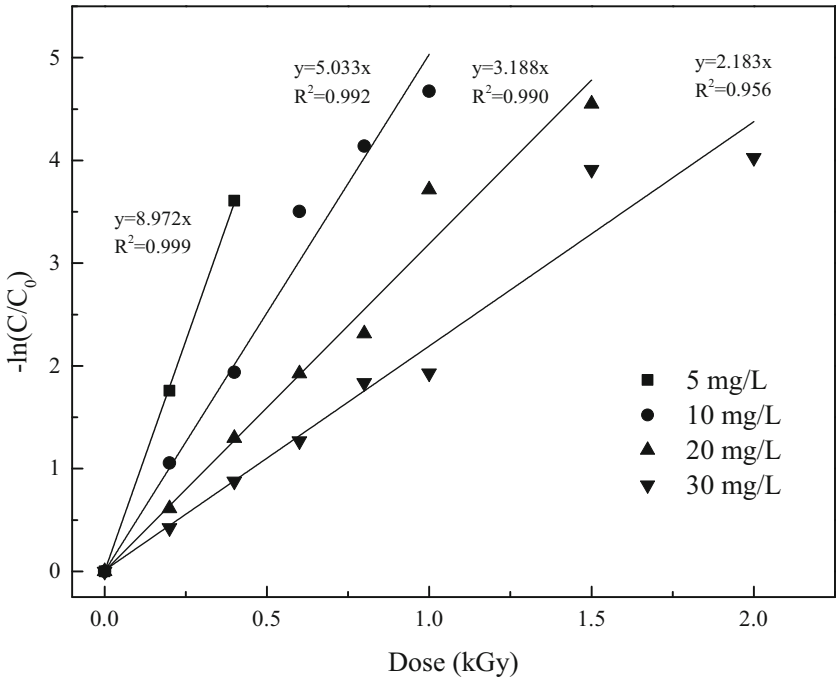


Fig. 3 The kinetics of SMX degradation at different initial concentration in the presence of Fe_3O_4 ($[Fe_3O_4]_{add}$ = 0.1 g/L)

H_2O_2, as represented in Eq. (1).

$$H_2O \rightarrow OH\ (2.7) + e_{aq}^{-}(2.6) + H\cdot\ (0.55) + H_2\ (0.45) + H_2O_2\ (0.71) + H_3O^{+}(2.6) \quad (1)$$

The numbers in bracket express the numbers of the reactive species formed when absorbed 100 eV energy.

Fe_3O_4 magnetic particles can react with H_2O_2 to generate hydroxyl radicals (·OH), as shown in Eqs. (2) and (3) (Song et al. 2006). Fe (II) was oxidized by H_2O_2 and produce hydroxyl radicals (·OH) on the surface of Fe_3O_4 magnetic particles. These hydroxyl radicals (·OH) could attack and destroy SMX molecules, finally promoted the degradation efficiency. Hou et al. (2016) observed that in heterogeneous catalytic system of Fe_3O_4/ H_2O_2, 72.2% of tetracycline was removed, and the generation of ·OH from the heterogeneous active site (≡Fe (II)) through reaction with H_2O_2 played an important role. Huang et al. (2012) reported that the removal efficiency of bisphenol A was over 80% in Fe_3O_4/H_2O_2 system, and

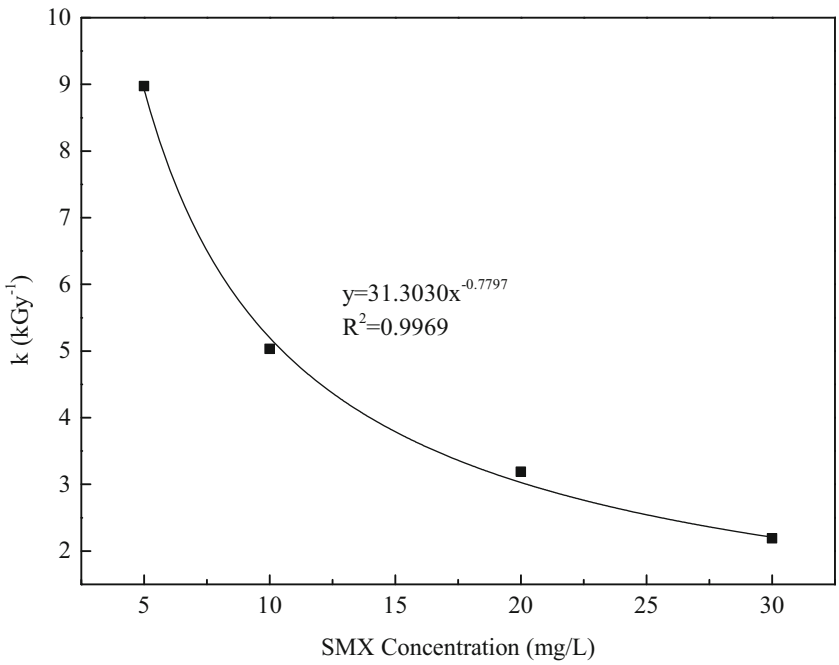


Fig. 4 Effect of initial SMX concentration on dose constant

Table 1 Dose constant with and without Fe_3O_4 addition

SMX initial concentration (mg/L)	Fe_3O_4 concentration (g/L)	Dose constant, k (kGy^{-1})	R^2
5	0.1	8.972	0.997
10	0.1	5.033	0.965
20	0.1	3.188	0.991
30	0.1	2.183	0.989
5	0	7.725	0.999
10	0	5.083	0.969
20	0	2.834	0.966
30	0	2.035	0.943

found that the Fe_3O_4 magnetic nanoparticles could catalyze H_2O_2 to form ·OH and then promote the degradation of bisphenol A. Xu and Wang (2012a) found that ·OH which formed on the surface of magnetic nanoparticles played a major role in 2,4-dichlorophenol degradation.

$$\equiv Fe(II) + H2O2 \rightarrow \equiv Fe(III) + \cdot OH + OH- \quad (2)$$

$$\equiv Fe(III) + H2O2 \rightarrow \equiv Fe(II) + H + + HO2- \quad (3)$$

Figure 2 exhibited the results of SMX degradation at various initial SMX concentrations in the presence of Fe_3O_4 under ionizing radiation. The initial concentration of SMX had apparent influence on its degradation rate by gamma irradiation. SMX degradation efficiency decreased when SMX concentration increased. With 0.6 kGy irradiation, SMX removal efficiency was 100.0%, 97.0%, 85.4%, and 71.8%, respectively when the initial concentration was 5, 10, 20, and 30 mg/L. The degradation efficiency was 45.7%, 72.6%, 85.4%, 90.1%, 97.6%, 98.9%, and 100.0% at SMX initial concentration of 20 mg/L with 0.2, 0.4, 0.6, 1.0, 1.5, and 2 kGy irradiation, respectively. It was reported that SMX removal percentage decreased from 100 to 91.3% when its concentration increased from 1 to 5 mg/L (Wang et al. 2017). Kim et al. (2017) also observed that degradation of SMX decreased with increase of its initial concentration.

The pseudo first-order reaction kinetic model (Eqs. 4 and 5) was applied to fit the SMX degradation process.

$$C = C_0 e^{-kD} \quad (4)$$

$$-ln\frac{C}{C_0} = kD \quad (5)$$

where C_0 is initial SMX concentration (mg/L); C is the residual SMX concentration after irradiation (mg/L); D is the absorbed dose (kGy); and k is the dose constant (kGy^{-1}).

It is obvious that $-\ln(C/C_0)$ increased linearly with the absorbed dose, with the correlation coefficient higher than 0.95, suggesting that the degradation of SMX followed

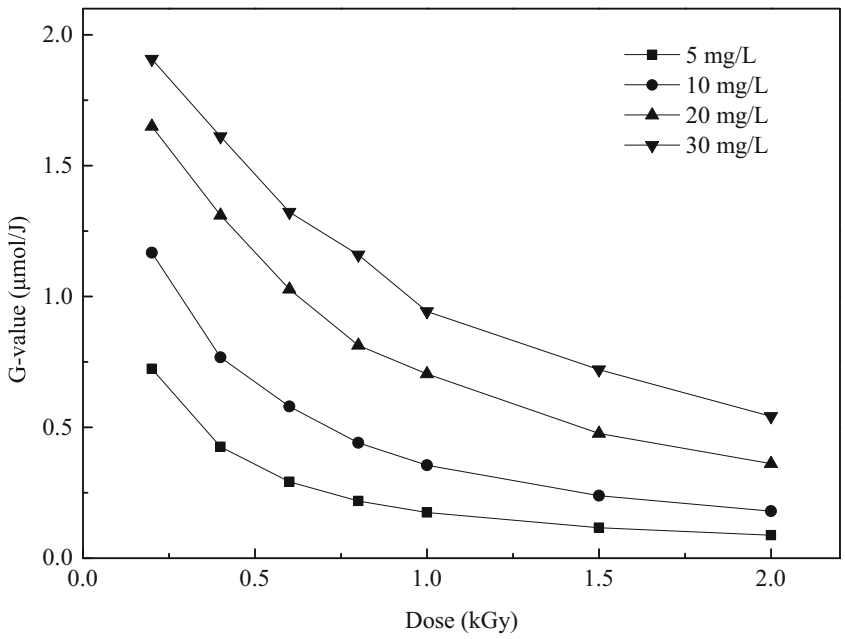


Fig. 5. Changes of G-value during SMX degradation

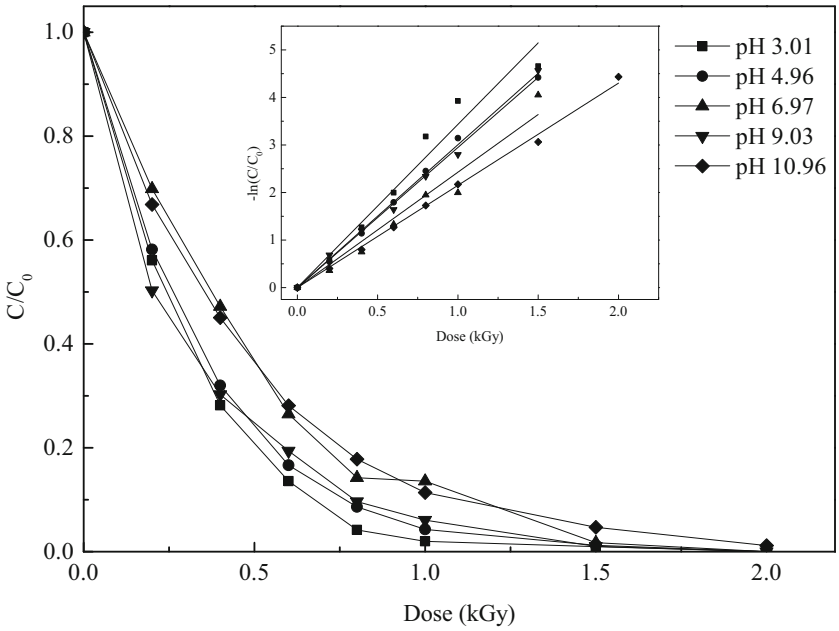


Fig. 6. Effect of pH on SMX degradation ($[SMX]_0$ = 20 mg/L)

pseudo-first-order kinetics model (Fig. 3). The dose constants were 8.972, 5.033, 3.188, and 2.183 kGy^{-1} at 5, 10, 20, and 30 mg/L, respectively. The relation between dose constant and the initial SMX concentration could be described by power function as Eq. (6) and illustrated in Fig. 4.

$$k = 31.3030\ C_0^{-0.7797}\quad R^2 = 0.9969 \tag{6}$$

This power function ($R^2 > 0.99$) revealed that dose constant was strongly related to initial SMX concentration. The dose constants (k) declined with increase of initial concentration of SMX. At higher initial concentration of SMX, more intermediate products were generated during ionizing irradiation, which inevitably consumed more reactive species. Thus, the effective collision between SMX molecules and these reactive radicals decreased (Wang et al. 2017; Shah et al. 2016). Based on the dose constant k (kGy^{-1}) shown in Table 1, the addition of Fe_3O_4 magnetic particles slightly enhanced dose constant k of SMX degradation by gamma irradiation. This could be due to that Fe_3O_4 magnetic particles accelerated the decomposition of H_2O_2 to generate ·OH radicals.

The radiation chemical yield (G) represents the number of particles including molecules, ions, and radicals formed or decomposed when absorbing 100 eV energy. According to Eq. (7), G-value was calculated as the number of molecules in micromole (μmol) produced or consumed when receiving 1 J of irradiation energy (Shah et al. 2014).

$$G\text{–value} = \frac{[R]}{D} \times 1.0 \times 10^6\ \mu\text{mol/J} \tag{7}$$

where D is the absorbed dose (Gy), and R was the change of the reactant concentration (mol/L).

Figure 5 showed the change of G-values at various initial SMX concentrations after ionizing irradiation. The G-value increased with increasing initial concentration for a certain absorbed dose. When initial SMX concentration increased, it would allow more chances for the reaction between the reactive radicals and SMX molecules, leading to higher G-values.

Basfar et al. (2005) observed that G-values decreased as the concentration of methyl tert-butylether (MTBE) decreased during gamma irradiation. Sayed et al. (2016) observed the similar results in the research of radiation-induced degradation of ciprofloxacin. More active radicals and the intermediate products were produced with an increase of absorbed dose. First of all, the competition between SMX parent molecules and intermediate products for reactive radicals might result in the decline of G-value (Sayed et al. 2016). Besides, this trend can be caused by the recombination of reactive radicals, as given by Eqs. (8)–(11) (Yu et al. 2008; Zheng et al. 2011).

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \quad \left(k = 5.5 \times 10^9 L/(\text{mol s})\right) \tag{8}$$

$$\cdot OH + e_{aq}^- \rightarrow OH^- \quad \left(k = 3.0 \times 10^{10} L/(\text{mol s})\right) \tag{9}$$

$$\cdot OH + \cdot H \rightarrow H_2O \quad \left(k = 7.0 \times 10^9 L/(\text{mol s})\right) \tag{10}$$

$$H_2O + \cdot H + e_{aq}^- \rightarrow H_2 + OH^- \quad \left(k = 2.5 \times 10^{10} L/(\text{mol s})\right) \tag{11}$$

Moreover, the competition between reactive radicals for SMX molecules increased with the increase of absorbed dose, which led to decrease of G-values (Sayed et al. 2016; Yu et al. 2008). The similar result was reported for the decomposition of various pollutants by gamma irradiation, such as cefaclor (Yu et al. 2008), methyl tert-butyl ether (MTBE) (Basfar et al. 2005), and ciprofloxacin (Sayed et al. 2016).

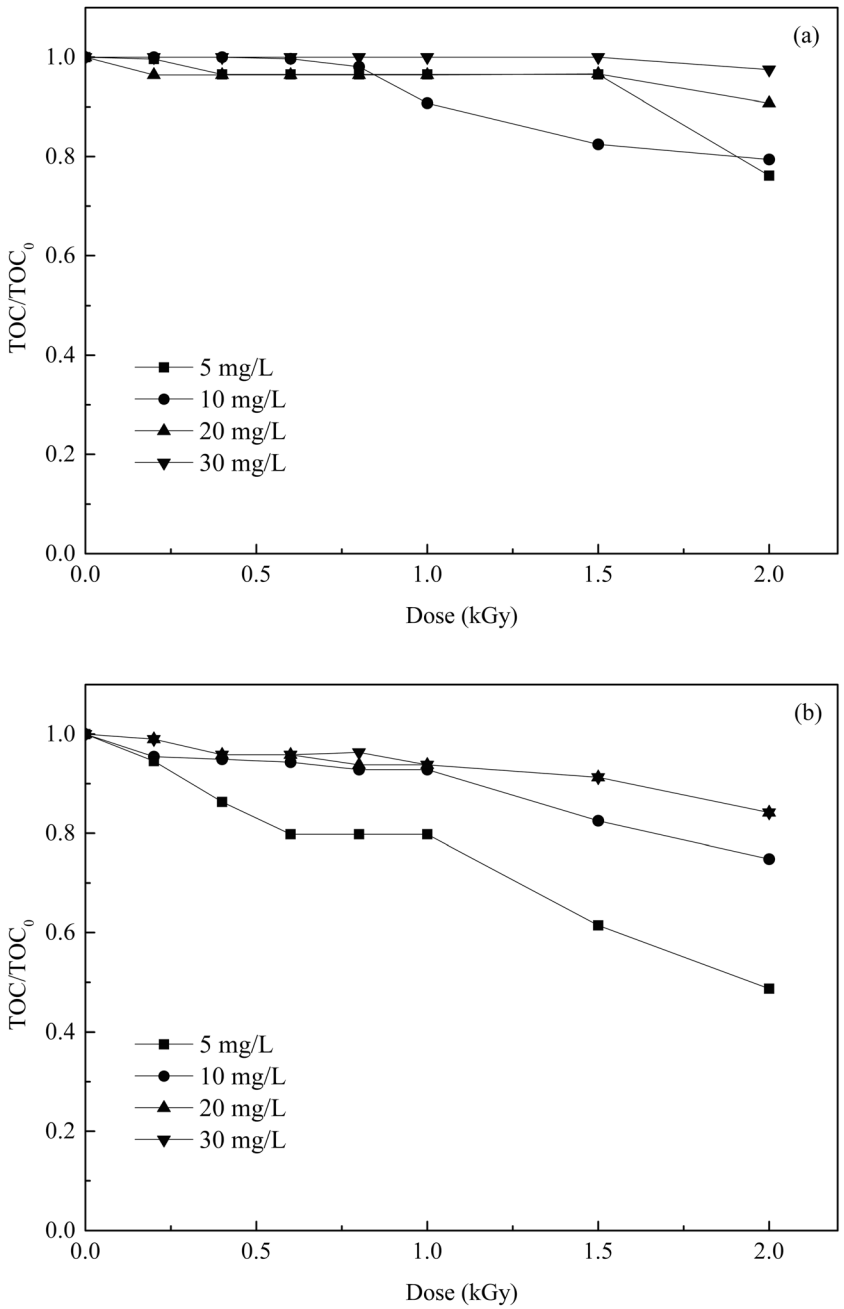


Fig. 7 Mineralization of SMX at different initial concentration during ionizing radiation **a** control, **b** with the addition of Fe_3O_4 $[Fe_3O_4]_{add}$ = 0.1 g/L)

Effect of pH on SMX degradation

For exploring the impact of pH on SMX degradation by irradiation, SMX solution at various initial pH values ranging from 3.01 to 10.96 was irradiated. Figure 6 illustrated the effect of pH on SMX degradation and the pseudo-first-order kinetic plots during SMX radiolytic degradation at different pH values.

SMX could be degraded in a wide range of pH values, and the degradation efficiency was more than 98%. The degradation rate constant was 3.432, 3.006, 2.428, 2.948, and 2.151 kGy^{-1} at pH 3.01, 4.96, 6.97, 9.03, and 10.96, respectively. It can be seen that acidic condition was more suitable for SMX degradation. The pH values determined the concentration of H^+ and OH^- in aqueous solution, thereby affecting the active radical composition formed during water radiolysis by Eqs. (12)–(14).

$$OH + OH^- \rightarrow \cdot H_2O + O \cdot^- \quad (12)$$

$$e_{aq}^- + \cdot OH \rightarrow OH^- \quad (13)$$

$$e_{aq}^- + H^+ \rightarrow \cdot H \quad (14)$$

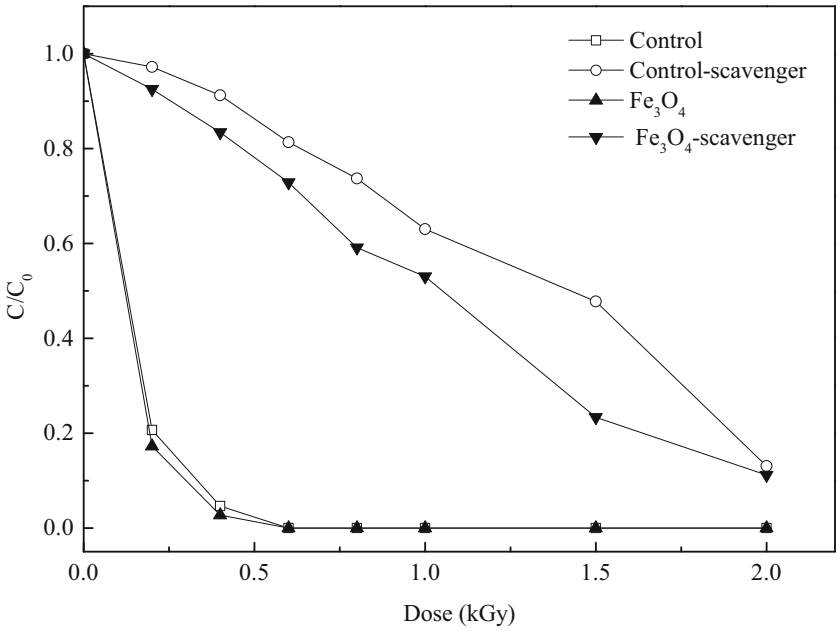


Fig. 8 Degradation of SMX in the presence of scavenger ($[SMX]_0$ = 20 mg/L, $[Fe_3O_4]_{add}$ = 0.1 g/L, [TBA] = 100 mM)

At alkaline condition, OH^- can easily react with ·OH radicals, thus decreasing the reaction rate, which was in agreement with the previous studies in the degradation of ofloxacin (Changotra et al. 2019) and sulfadiazine (Guo et al. 2012).

Mineralization of sulfamethoxazole

Unlike the complete removal of SMX, ionizing radiation process cannot achieve complete mineralization of SMX, as shown in Fig. 7. When the absorbed dose was less than 1 kGy, the TOC removal efficiency for 5 mg/L SMX changed slowly and reached 20.2%, while SMX could be degraded completely, as illustrated in Fig. 7(a). In this stage, SMX degraded into small molecular weight compounds. When absorbed dose increased to 2.0 kGy, the TOC removal efficiency gradually improved and reached the highest (51.3%), which can be explained by small molecular weight compounds gradually degrading into CO_2 and H_2O.

The similar results were obtained in previous researches on the degradation of BPA by heterogeneous sono-Fenton

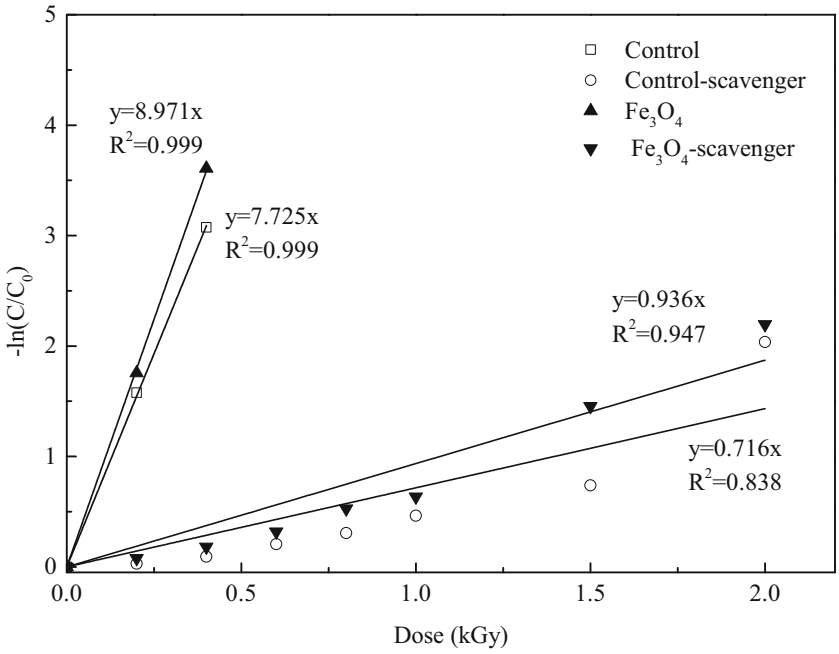


Fig. 9 The kinetics of SMX degradation in the presence of scavenger ($[SMX]_0$ = 20 mg/L, $[Fe_3O_4]_{add}$ = 0.1 g/L, [TBA] = 100 mM)

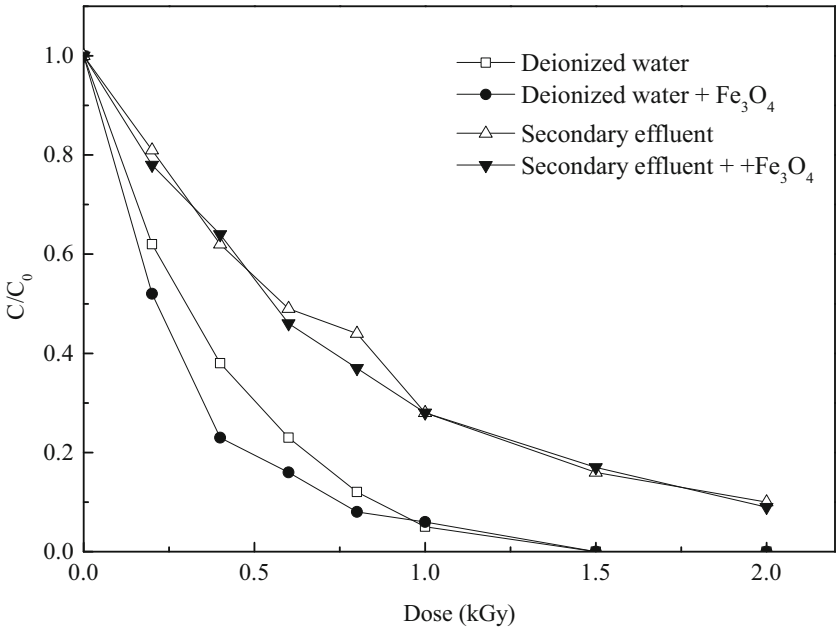


Fig. 10 Effect of water matrix on SMX degradation ($[SMX]_0$ = 20 mg/L, COD = 33.1 mg/L)

(Huang et al. 2014), by the Fenton-like degradation of 2,4-DCP (Xu and Wang 2012b). The remaining TOC may relate to some small molecular intermediate products, such as refractory organic acids generated from SMX degradation (Yang et al. 2015; Niu et al. 2011). As shown in Fig. 7(b), with the addition of Fe_3O_4 during the radiation process, TOC removal efficiency enhanced from 23.8 to 51.3% in comparison with the control group which was absence of Fe_3O_4 when SMX initial concentration was 5 mg/L. Fe_3O_4 may react with H_2O_2 which was formed during water radiolysis process, which generated more ·OH radicals, finally resulting in the improvement of TOC removal.

Role of ·OH radicals in sulfamethoxazole degradation

In order to investigate the role of ·OH radical in the SMX degradation process by gamma radiation, 100 mM tert-butyl alcohol was added as ·OH radical scavenger in SMX solution before irradiation because tert-butyl alcohol can react with ·OH according to the following Eq. (15).

$$\mathrm{OH} + \mathrm{t\text{–}BuOH} \rightarrow \cdot \mathrm{CH_2C(CH_3)_2OH} + \mathrm{H_2O}\ k = 6/0 \times 10^8\ (\mathrm{L}/(\mathrm{mol}\cdot\mathrm{s})) \quad (15)$$

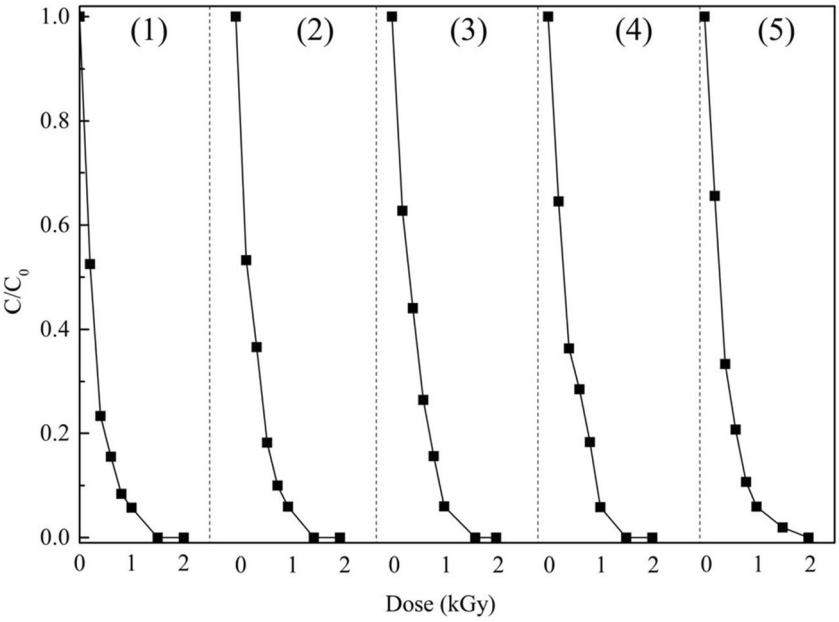


Fig. 11 Reusability of Fe_3O_4 catalyst under gamma irradiation. ($[SMX]_0$ = 20 mg/L, $[Fe_3O_4]_{add}$ = 0.1 g/L)

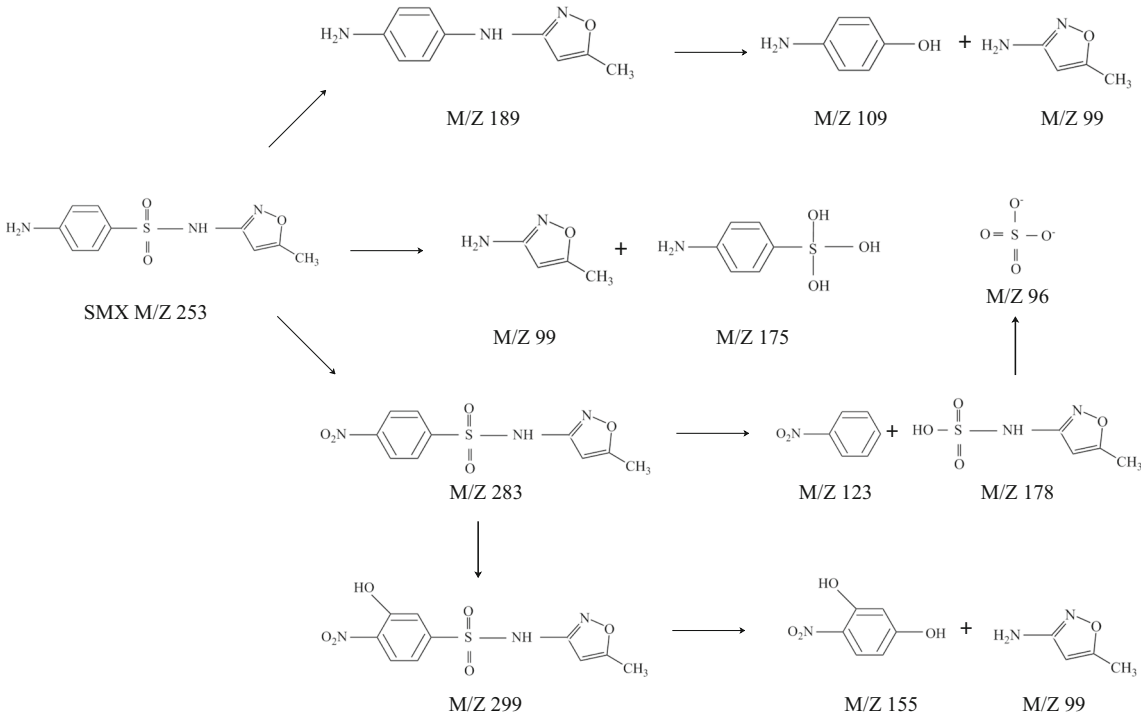


Fig. 12 Proposed pathway of SMX degradation under ionizing radiation

As illustrated in Fig. 8, the SMX degradation efficiency declined from 100 to 47% and 37% with and without the addition of Fe_3O_4 at the dose of 1 kGy.

The corresponding dose constants were calculated by pseudo-first-order kinetic plots as follows:

$$k\ (\text{control}) = 7.725\ \text{kGy}^{-1}$$

$$k\ (\text{control–scavenger}) = 0.716\ \text{kGy}^{-1}$$

$$k\ (\text{Fe}_3\text{O}_4) = 8.972\ \text{kGy}^{-1}$$

$$k\ (\text{Fe}_3\text{O}_4\text{–scavenger}) = 0.936\ \text{kGy}^{-1}$$

So, the dose constants for ·OH radical can be calculated as:

$$k\ (\text{control–OH}) = k\ (\text{control}) - k\ (\text{control–scavenger})$$
$$= 7.725 - 0.716 = 7.009\ \text{kGy}^{-1}$$

$$k\ (\text{Fe}_3\text{O}_4 - \cdot\text{OH}) = k\ (\text{Fe}_3\text{O}_4) - k\ (\text{Fe}_3\text{O}_4\text{–scavenger})$$
$$= 8.972 - 0.936 = 8.036\ \text{kGy}^{-1}$$

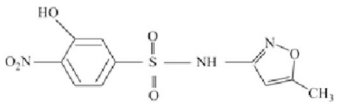
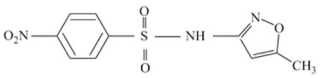
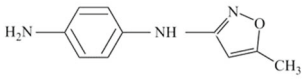
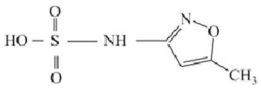
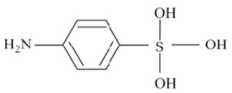
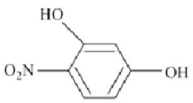
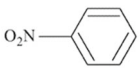
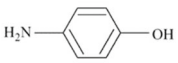
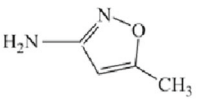
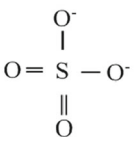
These calculated results revealed that with addition of 0.1 g/L Fe_3O_4, the dose constant of ·OH enhanced from 7.009 to 8.036 kGy^{-1} compared with the control group (Fig. 9). Thus, with the addition of Fe_3O_4, more ·OH radicals were formed, resulting in higher removal efficiency of SMX and TOC. Huang et al. (2012) also found that the reactive rate decreased remarkably from 7.96×10^{-3} min^{-1} (without t-BuOH) to 1.52×10^{-3} min^{-1} in the presence of 0.1 M t-BuOH during degradation of bisphenol A, indicating that Fe_3O_4 could excite H_2O_2 to form ·OH radicals. Zhang et al. (2009) applied Fe_3O_4 magnetic nanoparticles to degrade phenol and aniline in Fenton reaction, they found that the addition of tert-butyl alcohol inhibited the reactive rate and degradation efficiency, indicating that ·OH radicals played a responsible role in decomposition of phenol and aniline. Our previous study also indicated that Fe_3O_4-Mn_3O_4 could be used as Fenton-like catalyst for the degradation of sulfamethazine (Wan and Wang 2017)

Effect of water matrix on SMX degradation

Considering the practical application, the degradation of SMX in the secondary effluent of WWTP (wastewater treatment plant) by ionizing radiation was explored. Compared with SMX degradation in deionized water, SMX degradation efficiency decreased from 100 to 84% in secondary effluent (in Fig. 10). The substances such as anions and organic compounds in the secondary effluent could compete reactive species with antibiotic molecules, finally inhibiting the degradation efficiency (Peñalver et al. 2013).

Zhuan and Wang (2019) found that anions and organic matters in the solution had negative influence on degradation of SMX by gamma radiation. The presence of some common anions in real water such as CO_3^{2-}, HCO_3^-, NO_3^-, SO_4^{2-}, Cl^-, and HPO_4^{2-} could inhibit the

Table 2 Intermediate products of SMX degradation by ionizing radiation

M/Z	Chemical Structures	Proposed Formula
299		$C_{10}H_9N_3O_6S$
283		$C_{10}H_9N_3O_5S$
189		$C_{10}H_{11}N_3O$
178		$C_4H_6N_2O_4S$
175		$C_6H_9NO_3S$
155		$C_6H_5NO_4$
123		$C_6H_5NO_2$
109		C_6H_7NO
99		$C_4H_6N_2O$
96		SO_4^{2-}

degradation of SMX by radiation, because these anions could scavenge OH· and lead to a decrease of OH· concentration in the solution (Wang and Wang 2019). Adding organic matters also inhibited SMX degradation for their competition with SMX molecule to react with OH·.

Reusability of Fe_3O_4

The reusability of catalysts is important for their practical application. The reusability performance of Fe_3O_4 was illustrated in Fig. 11. Fe_3O_4 was used in the reaction solution for 5 cycles, and SMX was added repeatedly after each cycle under gamma irradiation. With 2 kGy radiation, SMX could be completely degraded after each cycle. Fe_3O_4 performed efficient reusability and stability for 5 cycles. Therefore, Fe_3O_4 was stable in gamma radiation process for the removal of antibiotics.

Degradation of intermediate products and pathway

Ionizing radiation is very effective for the degradation of organic pollutants; however, it is not efficient for their mineralization. Some degradation intermediate products formed during the radiation process, which were persistent after the total

removal of the parent compounds (Fig. 12). Thus it is needed to identify the intermediate products generated during ionizing radiation. The intermediate products of SMX degradation by radiation treatment were identified by liquid chromatography (LC)–mass spectrometry (MS) (Table 2). The intermediate product at *m*/*z* of 283 corresponded to the oxidation of amino group at benzene ring, which was also identified in the research of ozone oxidation sulfamethoxazole (Gomez-Ramos et al. 2011), sulfamethoxazole removal by Fenton process (Wang and Wang 2017), radiolytic degradation of sulfamethoxazole (Kim et al. 2017).

As for the intermediate product at *m*/*z* of 283, the breakage of the bond between sulfur and benzene ring might result in the generation of the intermediate products at *m*/*z* 123 and 178, respectively. The intermediate product at *m*/*z* 299 may be the product of adding a ·OH to the aniline ring of nitrosulfamethoxazole at *m*/*z* 283. The intermediate product at *m*/*z* 299 was also detected during the process of SMX degradation by Fenton oxidation (Wang and Wang 2017) and by ozone oxidation treatment (Abellan et al. 2008). The fragments at *m*/*z* 155 and *m*/*z* 99 may be due to the cleavage of the intermediate product at *m*/*z* of 299. The fragment at *m*/*z* of 189 could be the desulfurated product of SMX, as the loss of SO_2 ions from SMX molecule under the oxidation of ·OH. This SO_2 elimination and rearrangement pathway contained three steps: direct breakage of arylsulfone bond (C–S), direct breakage of sulfonamide bond (S–N), and SO_2 extrusion (Kim et al. 2017) Desulfonated intermediate products were also reported previously (Kim et al. 2017; Garcia-Galan et al. 2012; Boreen et al. 2005). Inorganic product at *m*/*z* 96 was identified as sulfate ion (SO_4^{2-}) during the degradation of SMX, which could be formed due to the cleavage of arylsulfone bond (C–S), such as the oxidation of intermediate product at *m*/*z* 178 (Kim et al. 2017).

Conclusion

Sulfamethoxazole can be efficiently degraded by ionizing radiation combined with Fenton-like process. The addition of Fe_3O_4 could enhance SMX degradation as well as dose constant compared with the control group. SMX degradation followed pseudo-first-order kinetic model, and its efficiency decreased with the increase of initial concentration. SMX could be degraded in a wide pH range. Over 98% of SMX were degraded at pH ranging from 3.01 to 10.96. Moreover, the presence of Fe_3O_4 could promote the mineralization of SMX. TOC removal efficiency increased from 23.8 to 51.3% with the addition of Fe_3O_4. The addition of free radical scavenger (tert-butyl alcohol) obviously inhibited SMX degradation, indicating that ·OH radicals played the main role in the SMX degradation in the radiation/Fe_3O_4 system. Fe_3O_4 could enhance dose constants of ·OH, suggesting that Fe_3O_4 could promote the form of ·OH radicals and enhance the degradation efficiency of SMX and TOC. The degradation efficiency of SMX in secondary effluent of WWTP decreased from 100 to 84% compared with that in deionized water. The intermediate products of SMX degradation were identified, and the possible degradation pathway was tentatively proposed.

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References

Abellan MN, Gebhardt W, Schroder HF (2008) Detection and identification of degradation products of sulfamethoxazole by means of LC/MS and -MS^n after ozone treatment. Water Sci Technol **58**:1803–1812

Basfar AA, Khan HM, Al-Shahrani AA, Cooper WJ (2005) Radiation induced decomposition of methyl tert-butyl ether in water in presence of chloroform: kinetic modelling. Water Res **39**:2085–2095

Boreen AL, Arnold WA, McNeill K (2005) Triplet-sensitized photodegradation of sulfa drugs containing six-membered heterocyclic groups: Identification of an SO^2 extrusion photoproduct. Environ Sci Technol **39**:3630–3638

Changotra R, Guin JP, Khader SA, Varshney L, Dhir A (2019) Electron beam induced degradation of ofloxacin in aqueous solution: kinetics, removal mechanism and cytotoxicity assessment. Chem Eng J **356**:973–984

Chen H, Wang JL (2019) Catalytic ozonation of sulfamethoxazole over Fe_3O_4/Co_3O_4 composites. Chemosphere **234**:14–24

Chen K, Zhou JL (2014) Occurrence and behavior of antibiotics in water and sediments from the Huangpu River, Shanghai, China. Chemosphere **95**:604–612

Chu LB, Zhuang ST, Wang JL (2018) Degradation kinetics and mechanism of penicillin G in aqueous matrices by ionizing radiation. Radiat Phys Chem **145**:34–38

Dantas RF, Contreras S, Sans C, Esplugas S (2008) Sulfamethoxazole abatement by means of ozonation. J Hazard Mater **150**:790–794

Gao L, Zhuang J, Nie L, Zhang J, Zhang Y, Gu N, Wang T, Feng J, Yang D, Perrett S (2007) Intrinsic peroxidase-like activity of ferromagnetic nanoparticles. Nat Nanotechnol 2(9):577–583

Garcia-Galan MJ, Diaz-Cruz MS, Barcelo D (2012) Kinetic studies and characterization of photolytic products of sulfamethazine, sulfapyridine and their acetylated metabolites in water under simulated solar irradiation. Water Res **46**:711–722

Gobel A, Thomsen A, McArdell CS, Joss A, Giger W (2005) Occurrence and sorption behavior of sulfonamides, macrolides, and trimethoprim in activated sludge treatment. Environ Sci Technol **39**:3981–3989

Gomez-Ramos MD, Mezcua M, Aguera A, Fernandez-Alba AR, Gonzalo S, Rodriguez A, Rosal R (2011) Chemical and toxicological evolution of the antibiotic sulfamethoxazole under ozone treatment in water solution. J Hazard Mater **192**:18–25

Gros M, Petrovic M, Ginebreda A, Barcelo D (2010) Removal of pharmaceuticals during wastewater treatment and environmental risk assessment using hazard indexes. Environ Int **36**:15–26

Guo Z, Fei Z, Zhao Y, Zhang C, Liu F, Bao C, Lin M (2012) Gamma irradiation-induced sulfadiazine degradation and its removal mechanisms. Chem Eng J **191**:256–262

Hou LW, Wang LG, Royer S, Zhang H (2016) Ultrasound-assisted heterogeneous Fenton-like degradation of tetracycline over a magnetite catalyst. J Hazard Mater **302**:458–467

Hu J, Wang JL (2007) Degradation of chlorophenols in aqueous solution by gamma-radiation. Radiat Phys Chem 76:1489–1492

Huang RX, Fang ZQ, Yan XM, Cheng W (2012) Heterogeneous sono-Fenton catalytic degradation of bisphenol A by Fe_3O_4 magnetic nanoparticles under neutral condition. Chem Eng J **197**:242–249

Huang RX, Fang ZQ, Fang XB, Tsang EP (2014) Ultrasonic Fenton-like catalytic degradation of bisphenol A by ferroferric oxide (Fe_3O_4) nanoparticles prepared from steel pickling waste liquor. J Colloid Interface Sci **436**:258–266

Karthikeyan KG, Meyer MT (2006) Occurrence of antibiotics in wastewater treatment facilities in Wisconsin, USA. Sci Total Environ **361**: 196–207

Khan S, Han C, Sayed M, Sohail M, Jan S, Sultana S, Khan HM, Dionysiou DD (2019) Exhaustive photocatalytic Lindane degradation by combined simulated solar light-activated nanocrystalline TiO_2 and inorganic oxidants. Catalysts **9**:425

Kim HY, Kim TH, Cha SM, Yu S (2017) Degradation of sulfamethoxazole by ionizing radiation: Identification and characterization of radiolytic products. Chem Eng J **313**:556–566

Liu YK, Wang JL (2013) Degradation of sulfamethazine by gamma irradiation in the presence of hydrogen peroxide. J Hazard Mater **250**: 99–105

Liu Y, Wang JL (2019) Reduction of nitrate by zero valent iron (ZVI)-based materials: a review. Sci Total Environ **671**:388–403

Liu YK, Hu J, Wang JL (2014) Fe^{2+} enhancing sulfamethazine degradation in aqueous solution by gamma irradiation. Radiat Phys Chem **96**:81–87

Liu Y, Fan Q, Wang JL (2018) Zn-Fe-CNTs catalytic in situ generation of H_2O_2 for Fenton-like degradation of sulfamethoxazole. J Hazard Mater **342**:166–176

Mirzaei A, Chen Z, Haghighat F, Yerushalmi L (2017) Removal of pharmaceuticals from water by homo/heterogonous Fenton-type processes—a review. Chemosphere **174**:665–688

Niu HY, Zhang D, Zhang SX, Zhang XL, Meng ZF, Cai YQ (2011) Humic acid coated Fe_3O_4 magnetic nanoparticles as highly efficient Fenton-like catalyst for complete mineralization of sulfathiazole. J Hazard Mater **190**:559–565

Peñalver JJL, Pacheco CVG, Polo MS, Utrilla JR (2013) Degradation of tetracyclines in different water matrices by advanced oxidation/reduction processes based on gamma radiation. J Chem Technol Biotechnol **88**:1096–1108

Phan TPH, Managaki S, Nakada N, Takada H, Shimizu A, Anh DH, Viet PH, Suzuki S (2011) Antibiotic contamination and occurrence of antibiotic-resistant bacteria in aquatic environments of northern Vietnam. Sci Total Environ **409**:2894–2901

Rehman F, Sayed M, Khan JA, Shah NS, Khan HM, Dionysiou DD (2018) Oxidative removal of brilliant green by UV/$S_2O_8^{2-}$, UV/HSO_5^- and UV/H_2O_2 processes in aqueous media: a comparative study. J Hazard Mater **357**:506–514

Sayed M, Ismail M, Khan S, Tabassum S, Khan HM (2016) Degradation of ciprofloxacin in water by advanced oxidation process: kinetics study, influencing parameters and degradation pathways. Environ Technol **37**(5):590–602

Sayed M, Arooj A, Shah NS, Khan JA, Shah LA, Rehman F, Arandiyan H, Khan AM, Khan AR (2018) Narrowing the band gap of TiO_2 by co-doping with Mn^{2+} and Co^{2+} for efficient photocatalytic degradation of enoxacin and its additional peroxidase like activity: a mechanistic approach. J Mol Liq **272**:403–412

Sayed M, Gul M, Shah NS, Khan JA, Khan ZUH, Rehman F, Khan AR, Rauf S, Arandiyan H, Yang CP (2019) In-situ dual applications of ionic liquid coated Co^{2+} and Fe^{3+} co-doped TiO_2: superior photocatalytic degradation of ofloxacin at pilot scale level and enhanced peroxidase like activity for calorimetric biosensing. J Mol Liq **282**: 275–285

Shah NS, Khan JA, Nawaz S, Khan, HM (2014) Role of aqueous electron and hydroxyl radical in the removal of endosulfan from aqueous solution using gamma irradiation. J Hazard Mater **278**:40-48

Shah NS, Khan JA, Al-Muhtaseb AH, Sayed M, Khan HM (2016) Gamma radiolytic decomposition of endosulfan in aerated solution: the role of carbonate radical. Environ Sci Pollut Res **23**(12):12362–12371

Shah NS, Khan JA, Sayed M, Khan ZUH, Rizwan AD, Muhammad N, Boczkaj G, Murtaza B, Imran M, Khan HM, Zaman G (2018a) Solar light driven degradation of norfloxacin using as-synthesized Bi^{3+} and Fe^{2+} co-doped ZnO with the addition of HSO_5^-: toxicities and degradation pathways investigation. Chem Eng J **351**:841–855

Shah NS, Rizwan AD, Khan JA, Sayed M, Khan ZUH, Murtaza B, Lqbal J, Din SU, Imran M, Nadeem M, Al-Muhtaseb AH, Muhammad N, Khan HM, Ghauri M, Zaman G (2018b) Toxicities, kinetics and degradation pathways investigation of ciprofloxacin degradation using iron-mediated H_2O_2 based advanced oxidation processes. Process Saf Environ Prot **117**:473–482

Shah NS, Khan JA, Sayed M, Khan ZUH, Ali HS, Murtaza B, Khan HM, Imran M, Muhammad N (2019) Hydroxyl and sulfate radical mediated degradation of ciprofloxacin using nano zerovalent manganese catalyzed $S_2O_8^{2-}$. Chem Eng J **356**:199–209

Shen YP, Zhuan R, Chu LB, Xiang X, Sun H, Wang JL (2019) Inactivation of antibiotic resistance genes in antibiotic fermentation residues by ionizing radiation: exploring the development of recycling economy in antibiotic pharmaceutical factory. Waste Manag 84:141–146

Sichel C, Garcia C, Andre K (2011) Feasibility studies: UV/chlorine advanced oxidation treatment for the removal of emerging contaminants. Water Res **45**(19):6371–6380

Song WJ, Cheng MM, Ma JH, Ma WH, Chen CC, Zhao JC (2006) Decomposition of hydrogen peroxide driven by photochemical cycling of iron species in clay. Environ Sci Technol **40**(15):4782–4787

Tang JT, Wang JL (2018a) Fenton-like degradation of sulfamethoxazole using Fe-based magnetic nanoparticles embedded into mesoporous carbon hybrid as an efficient catalyst. Chem Eng J **351**:1085–1094

Tang JT, Wang JL (2018b) Metal organic framework with coordinatively unsaturated sites as efficient Fenton-like catalyst for enhanced degradation of sulfamethazine. Environ Sci Technol **52**:5367–5377

Tang JT, Wang JL (2019) MOF-derived three-dimensional flower-like FeCu@C composite as an efficient Fenton-like catalyst for sulfamethazine degradation. Chem Eng J **375**:122007

Trojanowicz M, Bartosiewicz I, Bojanowska-Czajka A, Kulisa K, Szreder T, Bobrowski K, Nichipor H, Garcia-Reyes JF, Nalecz-Jawecki G, Meczynska-Wielgosz S, Kisala J (2019) Application of ionizing radiation in decomposition of perfluorooctanoate (PFOA) in waters. Chem Eng J **357**:698–714

Wan Z, Wang JL (2017) Degradation of sulfamethazine using Fe_3O_4-Mn_3O_4 /reduced graphene oxide hybrid as Fenton-like catalyst. J Hazard Mater **324**:653–664

Wan Z, Hu J, Wang JL (2016) Removal of sulfamethazine antibiotics using Ce-Fe-graphene nanocomposite as catalyst by Fenton-like process. J Environ Manag **182**:284–291

Wang JL, Bai ZY (2017) Fe-Based Catalysts for heterogeneous catalytic ozonation of emerging contaminants in water and wastewater. Chem Eng J **312**:79–98

Wang JL, Chu LB (2016) Irradiation treatment of pharmaceutical and personal care products (PPCPs) in water and wastewater: an overview. Radiat Phys Chem **125**:56–64

Wang JL, Wang SZ (2016) Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: a review. J Environ Manag **182**:620–640

Wang SZ, Wang JL (2017) Comparative study on sulfamethoxazole degradation by Fenton and Fe (II)-activated persulfate process. RSC Adv **7**(77):48670–48677

Wang JL, Wang SZ (2018a) Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. Chem Eng J **334**:1502–1517

Wang JL, Wang SZ (2018b) Microbial degradation of sulfamethoxazole in the environment. Appl Microbiol Biotechnol **102**:3573–3582

Wang SZ, Wang JL (2018c) Radiation-induced degradation of sulfamethoxazole in the presence of various inorganic anions. Chem Eng J **351**:688–696

Wang JL, Wang SZ (2019) Activation of peroxymonosulfate by sludge-derived biochar for the degradation of triclosan in water and wastewater. Chem Eng J **356**:350–358

Wang JL, Xu LJ (2012) Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application. Crit Rev Environ Sci Technol **42**:251–325

Wang JJ, Guo ZY, Shen XY, Guo QJ, Zhao YF, Zhu SN, Guo ZB (2017) Gamma irradiation-induced decomposition of sulfamethoxazole in aqueous solution: the influence of additives, biological inhibitory, and degradation mechanisms. Environ Sci Pollut Res **24**:23658–23665

Wang JL, Zhuan R, Chu LB (2019) The occurrence, distribution and degradation of antibiotics by ionizing radiation: an overview. Sci Total Environ **646**:1385–1397

Wardman P (1989) Reduction potentials of one-electron couples involving free-radicals in aqueous-solution. J Phys Chem Ref Data **18**: 1637–1755

Xu LJ, Wang JL (2011) A heterogeneous Fenton-like system with nanoparticulate zero-valent iron for removal of 4-chloro-3-methyl phenol. J Hazard Mater **186**:256–264

Xu LJ, Wang JL (2012a) Magnetic nanoscaled Fe_3O_4/CeO_2 composite as an efficient Fenton-like heterogeneous catalyst for degradation of 4-chlorophenol. Environ Sci Technol **46**:10145–10153

Xu LJ, Wang JL (2012b) Fenton-like degradation of 2,4-dichlorophenol using Fe_3O_4 magnetic nanoparticles. Appl Catal B Environ **123**: 117–126

Yang B, Tian Z, Zhang L, Guo YP, Yan SQ (2015) Enhanced heterogeneous Fenton degradation of methylene blue by nanoscale zero valent iron (nZVI) assembled on magnetic Fe_3O_4/reduced graphene oxide. J Water Process Eng **5**:101–111

Yu S, Lee B, Lee M, Cho IH, Chang SW (2008) Decomposition and mineralization of cefaclor by ionizing radiation: kinetics and effects of the radical scavengers. Chemosphere **71**(11):2106–2112

Yu SQ, Hu J, Wang JL (2010a) Gamma radiation-induced degradation of p-nitrophenol (PNP) in the presence of hydrogen peroxide (H_2O_2) in aqueous solution. J Hazard Mater **177**:1061–1067

Yu SQ, Hu J, Wang JL (2010b) Radiation-induced catalytic degradation of p-nitrophenol (PNP) in the presence of TiO_2 nanoparticles. Radiat Phys Chem **79**:1039–1046

Zhang SX, Zhao XL, Niu HY, Shi YL, Cai YQ, Jiang GB (2009) Superparamagnetic Fe_3O_4 nanoparticles as catalysts for the catalytic oxidation of phenolic and aniline compounds. J Hazard Mater **167**(1-3):560–566

Zheng BG, Zheng Z, Zhang JB, Luo XZ, Wang JQ, Liu Q, Wang LH (2011) Degradation of the emerging contaminant ibuprofen in aqueous solution by gamma irradiation. Desalination **276**(1-3):379–385

Zhuan R, Wang JL (2019) Degradation of sulfamethoxazole by ionizing radiation: Kinetics and implications of additives. Sci Total Environ **668**:67–73